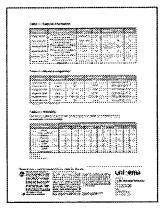
HypermerTM polymeric surfactants High molecular weight chemistry for ultimate performance







Unigema's Hypermer polymeric surfactants are molecules featuring repeating hydrophilic and hydrophobic units, designed to produce emulsions of high stability and controllable droplet size. The range of Hypermer products contained in this literature has been specifically selected for oilfield applications, where highest emulsification performance is required. Responding to the diverse technologies used in drilling, completion, stimulation, production and cleaning applications, Unigema's Hypermer range of oilfield surfactants combine a number of innovative base chemistries and emulsification mechanisms to readily produce water-in-oil or oil-in-water emulsions. All use steric

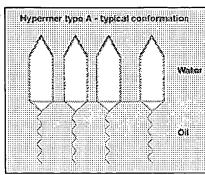


Figure 1

A - PEG Alkyds
Hydrophobe: Long-chain alkylene
Hydrophile: Polyethylene glycol

stabilization to form thermodynamically stable emulsions controlling flocculation, coagulation and coalescence effects.

These base chemistries of Hypermer surfactants are highly efficient interfacially active agents, yet they only marginally affect surface tension. Hypermer polymeric surfactants are non-ionic, however, the E type variant can behave as an anionic in suitably basic conditions. Hypermer surfactants are resistant to high ion concentrations, dispersed phase volumes and temperatures, meaning that highly stable emulsions can be produced with minimal foaming, even in paraffinic oils.

Following is a list of Uniquema's polymeric surfactants from the Hypermer range currently available for use in the oil and related industries. The generic chemistry, physical state and regulatory status are indicated. Please consult your local Uniquema representative for product lead times and for additional information.

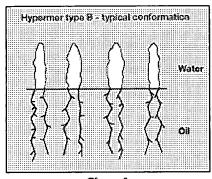


Figure 2

B-Block copolymer
Hydrophobe: Polyhydroxy fatty acid
Hydrophile: Polyethylene glycol

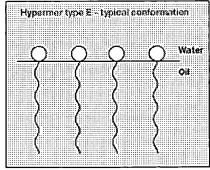


Figure 3

E-Oligomerics

Hydrophobe: Long-chain alkyšene Hydrophiše: Anionic/nonionic (various) FILE 'CAPLUS' ENTERED AT 09:09:44 ON 24 APR 2003
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FILE COVERS 1907 - 24 Apr 2003 VOL 138 ISS 17 FILE LAST UPDATED: 23 Apr 2003 (20030423/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

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200 HYPERMER
1 HYPERMERS
201 HYPERMER
(HYPERMER OR HYPERMERS)
3959 464
L1 2 HYPERMER (P) 464

=> s l1 and pluronic
4657 PLURONIC
269 PLURONICS
4755 PLURONIC

(PLURONIC OR PLURONICS)

L2 1 L1 AND PLURONIC

=> d 12 ti

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
TI Stable invert fuel emulsion compositions and method of making

=> d 12 all

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS

AN 1999:784208 CAPLUS

DN 132:13709

TI Stable invert fuel emulsion compositions and method of making

IN Coleman, Gerald N.; Endicott, Dennis L.; Jakush, Edward A.; Nikolov, Alex

PA Caterpillar Inc., USA

SO PCT Int. Appl., 39 pp.

CODEN: PIXXD2

DT Patent

LA English

IC ICM C10L001-32

CC 51-7 (Fossil Fuels, Derivatives, and Related Products)

FAN.CNT 1

PATENT NO. KIND DATE APPLICATION NO. DATE

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WO 1999-US12199 19990601
                        A1 19991209
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     WO 9963024
         W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO,
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PRAI US 1998-88060P
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     US 1998-88060
                              19990601
     WO 1999-US12199
                        W
     Method for producing high stability aq. fuel emulsions with an oil or fuel
AB
     continuous phase. The method provides for selectively combining
     prescribed quantities of diesel fuel, purified water, alc., and an
     additive package including a primary surfactant, a block copolymer, and a
     polymeric dispersant. The fuel emulsion is made by blending the diesel
     fuel and additive package, adding purified water to the fuel/additive
     mixt., aging the compn., and passing the aged compn. through a high shear
     mixer. The optimum stability in the oil continuous fuel emulsion is
     achieved by using a high shear mixing device, such as a Ross X-series
     Mixer Emulsifier, which results in the final fuel emulsion having a
     droplet size distribution of .apprx.1 .mu. or less.
ST
     diesel fuel emulsion
     Polymers, uses
TΤ
     RL: MOA (Modifier or additive use); USES (Uses)
         (block; stable invert fuel emulsion compns. and method of making)
TΤ
     Diesel fuel
     Dispersing agents
     Fuels
     Surfactants
         (stable invert fuel emulsion compns. and method of making)
IT
     Fatty acids, uses
     RL: MOA (Modifier or additive use); USES (Uses)
         (stable invert fuel emulsion compns. and method of making)
     Gasoline
IT
     RL: PEP (Physical, engineering or chemical process); PROC (Process)
         (stable invert fuel emulsion compns. and method of making)
   93-83-4
              106392-12-5, Pluronic 17R2
                                              154101-90-3,
IT.
     Hypermer E-464
     RL: MOA (Modifier or additive use); USES (Uses)
         (stable invert fuel emulsion compns. and method of making)
             THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE.CNT
RE
(1) Bertha Andras; WO 9812285 A 1998 CAPLUS
(2) British Petroleum Co PLC; EP 0301766 A 1989 CAPLUS
(3) Entoleter; WO 7900211 A 1979 CAPLUS
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(6) Peter-Hoblyn Jeremy, D; US 5584894 A 1996 CAPLUS
(7) Scheuermann Ted, W; US 5873916 A 1999 CAPLUS
=> FILE REG
COST IN U.S. DOLLARS
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                                                                      TOTAL
                                                          ENTRY
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                                                           9.44
FULL ESTIMATED COST
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)
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STRUCTURE FILE UPDATES: 23 APR 2003 HIGHEST RN 504385-01-7 DICTIONARY FILE UPDATES: 23 APR 2003 HIGHEST RN 504385-01-7

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2003

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Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STNote 27, Searching Properties in the CAS Registry File, for complete details: http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf

=> STR 154101-90-3

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=> s 154101-90-3/rn

L3 1 154101-90-3/RN

6

The ethyl alcohol combusts and the carbamic acid produced insitu decomposes readily to ammonia and carbon dioxide. The ammonia reduces the oxides of nitrogen. The ethyl carbamate is a component of the microemulsion fuel. The key to this concept is that the 5 ammonia is produced in the later stages of the combustion which is desirable.

(c) Use a combination of (a) and (b).

3. The concept that the sulfur in petroleum products such as diesel oil and fuel oil oxidize to sulfur oxides like sulfur 10 dioxide in the combustion chamber and the sulfur oxides combine with steam in the exhaust gases to produce sulfur acids such as sulfurous acid which pollutes the air. Further to this concept is that the combination of oxides of nitrogen and the sulfur acids result in acid rain which is detrimental 15 to vegetation.

The idea created is to stoichiometrically neutralize the sulfur acids generated in the combustion chamber by adding an alkaline substance like sodium bicarbonate or sodium carbonate to the microemulsion fuel.

The above objectives of this invention and the above concepts and ideas to achieve these objectives are embodied in the new and novel microemulsion fuel compositions by weight which are summarized as follows:

(a) Diesel oil or fuel oil comprising about 50 to 90% of the 25 microemulsion fuel.

(b) An anionic surfactant prepared from the partial neutralization of 60 to 70 mole percent of the unsaturated fatty acids with ammonia such that there results both free fatty acids and the ammonium salts of the fatty acids. The ammonium salts of the fatty acids which represent the anionic surfactant comprise about 4 to 12% by weight of the microemulsion fuel. The free fatty acids comprise about 2 to 6% by weight of the microemulsion.

(c) A non-ethoxylated non-ionic surfactant. The specific 35 surfactant, which is a novel part of this invention, is 2,4,7,9 tetramethyl-5-decyne-4,7 diol, manufactured by Air Products and Chemicals, Inc. under the trade name of Surfynol 104. When this surfactant is dissolved in 2-ethylhexanol-1 as a 50% solution by weight it is called Surfynol 104A. The surfactant and the solvent comprise about 1 to 2% each by weight of the microemulsion. This surfactant is also called "Acetylenic Diol Surfactant" which name will be used in the examples.

(d) Long chain water-insoluble or slightly soluble in water 45 aliphatic alcohols with melting points below 0° C., for example, octanol-1, comprising 2 to 8% by weight of the microemulsion.

- (f) Water-soluble aliphatic alcohols such as methanol and ethanol comprising about 5 to 14% of the microemulsion fuel.
- (g) Total water in the microemulsion comprising about 1 60 to 10% of the microemulsion fuel.
- (h) Urea NOx scavenger comprising about 0.1 to 4.0% by weight of the microemulsion fuel.
- (i) Ethyl carbamate NOx scavenger comprising about 0.1 to 4.0% by weight of the microemulsion fuel.

The first step in the preparation of the water-in-oil microemulsion fuel is to prepare the solution of additives. In preparing this solution there is no particular order of adding the components except that the aqueous ammonia is added last. However, there is one exception to this. For solutions containing ethyl carbamate, the aqueous ammonia is added before the ethyl carbamate to assure that none of the ethyl carbamate will hydrolyze.

The second step is the mixing of the solution of additives with the petroleum product such as diesel oil. One of the advantages of the microemulsions of this invention is that only very low shear mixing is necessary to prepare the water-in-oil microemulsion fuels.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to low viscosity, stable (W/O) microemulsions prepared by mixing petroleum products such as diesel oil and fuel oil with a solution of additives. The microemulsions are crystal clear at room temperature but like diesel oil and heating fuel oil, they become hazy at sub-freezing temperatures but with the important characteristics that there is not any phase separation and that they have good fluidity like diesel oil itself.

The solution of additives is a clear, low viscosity and stable molecular solution. It is prepared separately and can be stored separately until ready to use when preparing the microemulsions fuel.

The microemulsion is readily prepared by mixing the petroleum product with the solution of additives at room temperature. On a large scale the microemulsion can be prepared by feeding the solution of additives and the petroleum product from the respective storage tanks through separate pipe lines into a common pipe line that leads to a storage tank for the microemulsion fuel. The flow rates are monitored to deliver the preferred blend of the solution of additives with the petroleum product. For example, a preferred blend of v/v 65/35 diesel oil/additive solution is 1.857 times the flow rate of the solution of additives for the same pipe diameter. The flow rates are readily maintained because of the low viscosities and easy transport of both the solution of additives and the diesel oil.

THE FUNDAMENTAL COMPONENTS OF THIS INVENTION

The solution of additives comprise six fundamental components described below.

- 1. An anionic surfactant prepared by the neutralization of 60 to 70% of the unsaturated fatty acids with ammonia such that there results both the ammonium salts of the fatty acids which represent the anionic surfactant and free fatty acids.
- 2. A non-ethoxylated non-ionic surfactant, the acetylenic diol surfactant, 2,4,7,9-tetramethyl-5-decyne-4,7-diol dissolved in 2-ethylhexanol-1.
- 3. Long chain, water-insoluble aliphatic alcohols with melting points below 0° C. such as octanol-1.
- 4. Water-soluble aliphatic alcohols such as methanol and ethanol.
 - 5. Water.
 - 6. NOx scavengers urea and ethyl carbamate..

Item 1

Unsaturated fatty acids derived from vegetable oils such as soybean oil which consist of oleic acid, linoleic acid and linolenic acid which comprise at least 90% of the fatty acids are used. Present in the unsaturated fatty acids are minor

U.36?